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Contrasting behaviour of trace metals in the Scheldt estuary in 1978 compared to recent years

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Abstract

Dissolved and particulate trace metals (Cu, Cd, Pb, Zn, Ni, Fe and Mn) measured at six stations along the Scheldt estuary in October/November 1978 are compared with more recent data. Based on Ca content in the suspended matter, three distinct geochemical regions could be distinguished: the upper estuary (salinity 1–7) dominated by fluvial mud, mid-estuary (salinity 7–17) where the composition of the suspended matter remained relatively constant, and the lower estuary where marine mud prevailed. Re-suspension of sediments is the major factor controlling the composition of the particles in the upstream region. Anoxic conditions prevailed in the upper part of the estuary extending to a salinity of 15 in 1978, while at present the seaward boundary of the anoxic water body is located at less saline waters. Furthermore, the present-day metal load is much lower than in 1978. As a consequence of the changed situation, maxima in dissolved concentrations of redox-sensitive metals in the mid/lower estuary have moved as well, which affects the trace metal re-distribution pattern. In the anoxic zone, exchange processes between dissolved and particulate metal fractions were strongly redox regulated, with Fe and Mn as excellent examples. Iron was removed from the dissolved phase in the early stages of mixing resulting in an increase in the suspended particulate matter of the leachable ‘non-residual’ Fe fraction from 2 to 3.5%. Due to its slower kinetics, removal of Mn from solution occurred in mid-estuary where oxygen concentrations increased. Cu, Cd and Zn on the contrary were mobilised from the suspended particles during estuarine mixing. External inputs of Pb, and to a lesser extent of Cu, in the lower estuary resulted in the increase of their particulate and the dissolved concentrations. Calculated K_d (distribution coefficient) values were used to assess the redistribution between the dissolved and particulate phase of the investigated metals. Due to the existence of the anoxic water body in the upper estuary, the importance of redox processes in determining the K_d values could be demonstrated. The sequence of K_d values in the upper estuary (Fe, Cd, Zn, Pb > Cu > Ni, Mn) is significantly different from that in the lower estuary (Fe > Mn > Pb, Ni, Zn, Cu, Cd). Thus, in such a dynamic estuary single metal-specific K_d values cannot be used to describe redistribution processes. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: River Scheldt; trace metals; water; suspended particulate matter; K_d values

1. Introduction

Estuaries are dynamic environments characterised by strong vertical and lateral gradients in salinity, pH,

suspended particulate matter (SPM), O_2 concentration and current velocities. These changes affect the distribution of trace metals over the dissolved and particulate phases with respect to source waters (Duinker et al., 1982a; Turner et al., 1993; Zwolsman and Van Eck, 1993; Turner, 1996; Paucot and Wollast, 1997).

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The most favourable estuaries to study these effects are those where the residence time of the water is long enough to reach chemical equilibrium.

One such estuary is that of the river Scheldt. The mean annual discharge of the water and suspended load amounts to $3.2 \times 10^9 \text{ m}^3$ and $0.4 \times 10^6 \text{ t}$, respectively (Valenta et al., 1986; Van Maldegem et al., 1993). In the estuary, the residual currents, measured in a cross-section over one complete tidal cycle, drop from 0.08 m s^{-1} at Durme 100 km upstream, to 0.02 m s^{-1} at Bath 50 km upstream of the river Scheldt (Wollast, 1988). The average residence time in the brackish water zone, which extends over 100 km, is between 1 and 3 months (Wollast, 1988). At the time of our study (1978), about two-thirds of the suspended load were related to anthropogenic activities and highly contaminated with heavy metals (Wollast, 1988). The particles, due to domestic and agricultural inputs, had an organic matter content as high as 40 to 60% by weight (Wollast, 1988), which led to almost anoxic conditions in the upstream mixing zone of the river due to intense mineralisation processes. Thus, oxidation and reduction processes dictated metal chemistry. At present, however, the organic matter content of the fluvial SPM is in the order of 10 to 15% (Van Maldegem et al., 1993).

Recently several articles have appeared describing the geochemistry of trace metals in the river Scheldt and its estuary (Zwolsman and Van Eck, 1990, 1993; Monteny et al., 1993; Regnier and Wollast, 1993; Stronkhorst, 1993; Paucot and Wollast, 1996, 1997; Zwolsman et al., 1997; Baeyens et al., 1998a,b). Most of these papers are based on samples collected along longitudinal sections, and only a few of the results were obtained at fixed tidal stations. Exchange processes of the metals are mostly explained by the changing oxidation and reduction conditions that occur in the estuarine mixing zone (Zwolsman and Van Eck, 1990, 1993; Monteny et al., 1993; Regnier and Wollast, 1993). Another approach to explaining trace metal desorption/mobilisation is the use of distribution coefficients (K_d , $\text{cm}^3 \text{ g}^{-1}$) (Turner et al., 1993). Monteny et al. (1993) and Paucot and Wollast (1996, 1997) applied this approach to the estuarine zone of the river Scheldt. Although part of the data (Mn, Cd, Ni, Zn) discussed in the present paper were published earlier (Duinker et al., 1982a), it is interesting, also in a historical context, to compare them with data pub-

lished recently. Due to the reduction of local inputs and the improvement of waste-water treatment, the anoxic zone has now moved upstream to a salinity of around 7 in summer (Zwolsman et al., 1997; Baeyens et al., 1998b). In winter, with high river discharges, the situation has improved to the extent that no anoxic zone exists in the upper estuary any more (Zwolsman et al., 1997; Baeyens et al., 1998b). With the information of the present situation in the Scheldt estuary and our historical data, it will be interesting to investigate which impact the changed situation has on the trace metal distributions. We present data for Cu, Pb, Cr, Fe and Al not published earlier and calculate K_d values to describe the complex trace metal behaviour in the river Scheldt.

A detailed description of the study area is given by Zwolsman et al. (1997) and will not be repeated in this paper. All data discussed here can be obtained from the authors on request.

2. Sampling and methods

Six 13-h-lasting tidal stations, covering the whole salinity regime from fresh to saline waters, in the Scheldt estuary (Fig. 1) were sampled with RV *Eider* of the Netherlands Institute for Sea Research (NIOZ) in October and November 1978. The sampling positions were selected in such a way that at most tidal stations the minimum or maximum salinity mea-

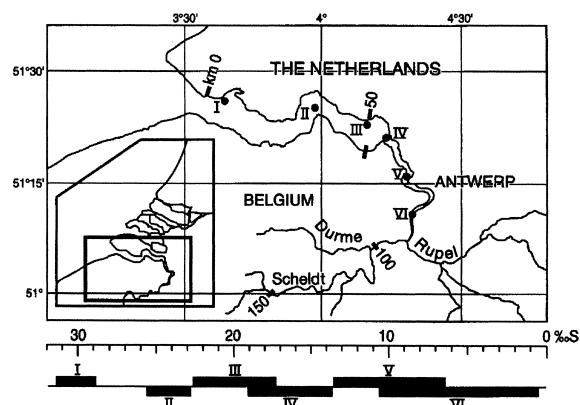


Fig. 1. Map of the river Scheldt with the six positions of the tidal stations. The bar indicates the salinity range observed at each station.

sured during one tidal cycle overlapped with those obtained at the adjacent stations (Fig. 1). Current velocities were highest at the surface at all stations, and varied from 1.2 m s^{-1} at station VI to 0.7 m s^{-1} at station I.

Water samples (1 dm^3) were collected at 1 m depth every hour and immediately filtered under nitrogen gas pressure over $0.45 \text{ }\mu\text{m}$ Supra Pur HCl washed Millipore cellulose nitrate filters in an all-teflon apparatus (Duinker and Nolting, 1977). Filtrate was collected in pre-cleaned polypropylene bottles and acidified to pH 2 with 1 cm^3 Supra Pur 12 N HCl. The filters + residue were washed with 50 cm^3 double quartz distilled water to remove sea-salts, dried at 70°C , and stored in petri dishes. Although all precautions were taken to avoid contamination, we have to keep in mind that at the time of this investigation sampling and processing were not as sophisticated as today. Therefore, contamination during sampling cannot be completely ruled out. However, taking into account the very high trace metal concentrations present in the Scheldt estuary during our research, such contamination would be of minor importance. Dissolved oxygen, temperature, pH and current velocities were measured continuously with a multi probe supplied by the Université Libre de Bruxelles.

Dissolved metals were determined after a pre-concentration-complexation treatment by graphite furnace atomic absorption spectroscopy (GFAAS). The metals were complexed with a mixture of 1% each of ammonium-pyrrolidine-dithiocarbamate (APDC), diethyl-ammonium-diethyl-dithiocarbamate (DDDC), and extracted into methyl isobutylketone (MIBK) in teflon separatory funnels. After phase separation the water was discarded, and the complexes in the MIBK were destroyed by adding 12 N nitric acid (Supra Pur), back extracted into 5 cm^3 double quartz distilled water, and stored in small teflon bottles (Kinrade and Van Loon, 1974; Danielsson et al., 1978). Standard additions were added to some water samples to determine the extraction efficiency, which was better than 90% for all metals investigated.

After drying and weighing the filters, they were combusted in a low temperature asher and the residue was extracted with 50 cm^3 0.1 N HCl. After 18 h the solutions were filtered over a $0.45 \text{ }\mu\text{m}$ acid washed

Millipore (cellulose nitrate) filter (Duinker et al., 1974). The filtrate with the ‘non-residual’ fraction was stored in 50-cm^3 volumetric flasks and the filters containing the residual fraction were digested with a hydrofluoric acid, aqua regia ($\text{HF-HNO}_3 : \text{HCl} : 1 : 3$) mixture in Teflon bombs at 110°C for two hours. After cooling, the solutions were stored in 50-cm^3 polypropylene volumetric flasks which contained 30 cm^3 saturated boric acid (H_3BO_3) as stabiliser (Rantala and Loring, 1977). With this procedure we obtained the ‘leachable’ (non-residual) and ‘residual’ fractions of the trace and major elements in the SPM. The sum of these two fractions presented the total metal content in the SPM. Differences between summing up of the two fractions and direct measurement of the total metal content SPM were studied and repeated for reference sediment samples in 1990, using the same methods as in 1978 (Van Hoogstraten and Nolting, 1991). It showed that for most elements this difference was less than 5%. Depending on their concentration in the final solution the metals were determined either by flame or graphite furnace AAS (Perkin Elmer 5000), while standard addition techniques were applied in order to compensate for matrix effect. The precision and accuracy for the determination of the elements in the SPM were extensively studied by inter-laboratory measurements, filtration and centrifugation, and different detection methods (AAS and neutron activation analysis, NAA) (Duinker et al., 1979a). The results of these inter-comparisons, in triplicate, showed that for the trace metals small differences occurred between filtration and centrifugation, due to particle-size effects, but that for the major elements no differences were found. Reproducibility of the analyses was between 6 and 12%, depending on the amount SPM per dm^3 .

3. Results and discussion

3.1. Suspended particulate matter

The amount of SPM (mg dm^{-3}), as measured over the entire tidal cycles is given in Fig. 2a. Maximum turbidity decreased sharply from about 300 mg dm^{-3} at low salinity to $30\text{--}80 \text{ mg dm}^{-3}$ at positions IV–II ($S > 15$). At positions VI and V the SPM changed

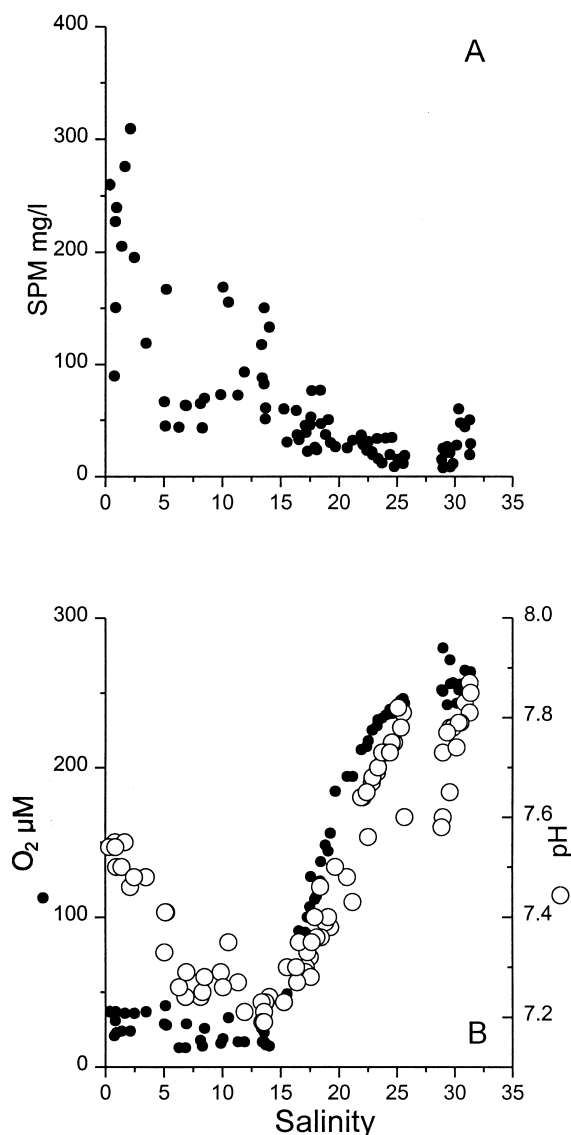


Fig. 2. Amount of (A) SPM and (B) pH and oxygen concentration in relation to salinity. All data obtained during the tidal cycles at each fixed position.

rapidly depending on current velocities. Maximum SPM concentrations occurred simultaneously with maximum currents probably as a result of resuspension of bottom sediments, and minimum values were observed at slack water.

Accumulation of sediments takes place in a 30-km-long zone (Fig. 1: km 55–85, near the port

of Antwerp) and is described in detail by Wollast (1988). Particularly in the upper estuary colloids may be important in addition to SPM (Duinker et al., 1982a).

3.2. Dissolved oxygen and pH

Dissolved O₂ was very low in the upper part of the estuary (stations VI and V) and values sharply increased at a $S > 15$ (Fig. 2b). These low O₂ concentrations are a result of the microbial degradation of organic matter using oxygen as an electron acceptor (Billen, 1975; Paucot and Wollast, 1997; Regnier et al., 1997). The extension of the area under anoxic conditions changes over the year due to differences in freshwater input, temperature and organic loading, and is smaller in winter periods (Zwolsman and Van Eck, 1993). Recent observations made by Zwolsman et al. (1997), Paucot and Wollast (1997) and Baeyens et al. (1998b) indicate that the anoxic area has moved from salinity 15 in 1978 to salinity < 7 –8 at present, thanks to improved waste-water treatment in the hinterland (Fig. 3).

The decrease of pH in the upper estuary (Fig. 2b) is mainly due to intense nitrification (Zwolsman and Van Eck, 1993; Regnier and Wollast, 1993; Paucot and Wollast, 1997; Zwolsman et al., 1997).

3.3. Characteristics of the suspended matter

We used the total Ca content of the suspended particles (Fig. 4a) to calculate the mixing ratio of SPM in different parts of the estuary. This approach was used earlier by Nolting et al. (1990) to differentiate between river- and marine-derived particles in the Rhine estuary. As indicated in Fig. 4a the Ca content of the SPM depends on the tidal period, and hence on the current velocity, especially downstream. For example, the Ca content in the SPM sampled during a complete tidal cycle at station I ($S \sim 30$) ranged from 6.3% during low tide to 10.1% at high tide. Taking a Ca content in the SPM of 4.4% at salinity 1.5 (Fig. 4a) and 10.3% for the marine material (salinity 33, Paalman, 1997), the distribution pattern of fluvial particles in the estuary as presented in Fig. 4b was calculated. This SPM distribution agrees well with the results of Salomons and Eysink (1981), using the difference in C^{12}/C^{13} ratios of fluvial and

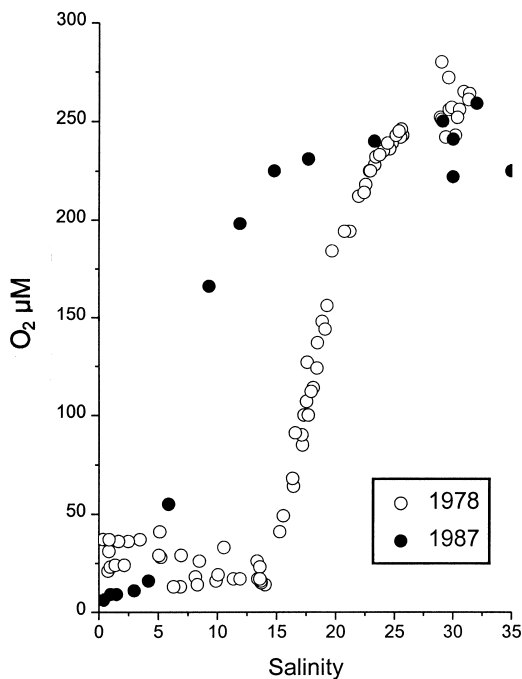


Fig. 3. Oxygen concentrations (μM) against salinity in October/November 1978 (this study) and in October 1987 (data Zwolsman et al., 1997).

marine SPM. Regnier and Wollast (1993) used Al as a tracer and produced almost the same distribution of SPM in terms of marine versus fluvial SPM. We also measured Al in the SPM, and although the concentrations were in the same range (4.0–5.0%) as those obtained by Regnier and Wollast (1993), we did not find a significant difference in Al content between marine and riverine end members; neither did Zwolsman and Van Eck (1999).

At low salinity the percentage of fluvial material decreases rapidly to about 70% (S 7), shows a weaker gradient between salinity 7 and 17, and then decreases to 10% at a salinity of 30. However, the distribution pattern of fluvial SPM versus salinity depends strongly on the river flow (Verlaan et al., 1998). So the positions of the zones may change during the year, but the pattern itself remains intact (Nihoul et al., 1978; Salomons and Eysink, 1981; Regnier and Wollast, 1993).

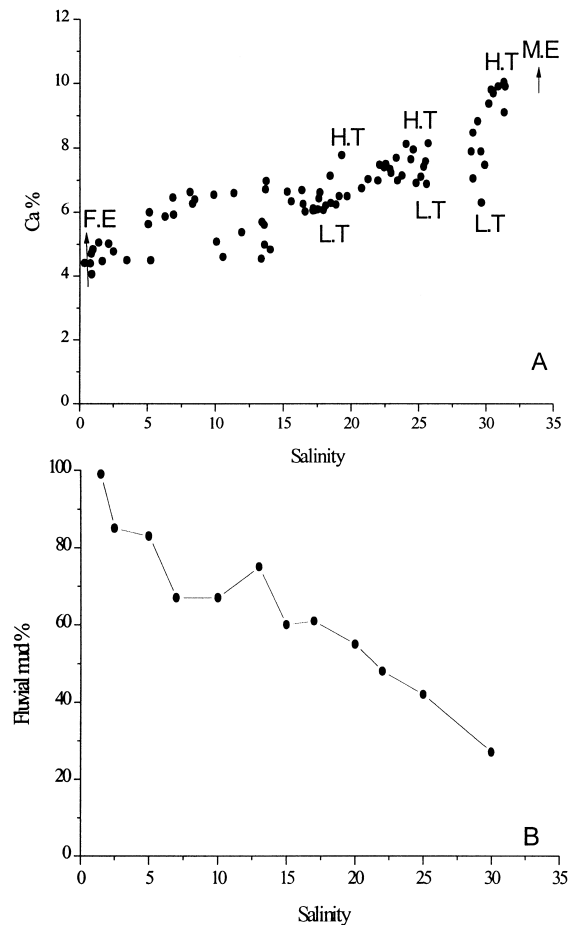


Fig. 4. (A) Calcium content in the SPM at the six stations. Samples collected at high tide (H.T) and low tide (L.T), the marine end member (M.E) and the fluvial end-member (F.E), indicated by the arrow are highlighted in the figure. (B) The percentage of fluvial material calculated with the Ca content in the SPM is presented as function of salinity.

3.4. Metal exchanges

The rapid removal of Fe from the dissolved phase in the early stages of estuarine mixing is well described for many estuaries (Sholkovitz, 1978; Duinker and Nolting, 1978; Figuères et al., 1978; Hunter and Leonard, 1988; Wen et al., 1999). Fig. 5a shows the leachable Fe fraction (as percent of SPM) and dissolved Fe. The oxidation of Fe into oxyhydroxides, with a subsequent removal from the dissolved phase, can be seen in Fig. 5a,b. Between salinity 3 and 7 the leachable Fe fraction (Fig. 5a),

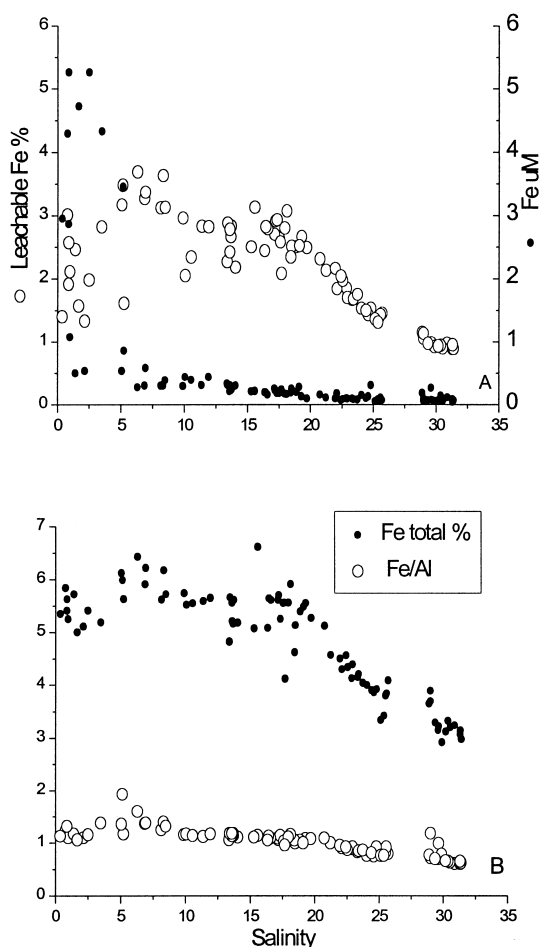


Fig. 5. (A) Dissolved Fe (μM) concentration and Fe % in the SPM (leachable fraction) against salinity. (B) Total Fe concentration in (%) and the Fe/Al ratio in the SPM.

the total Fe content and the Fe/Al ratio increase (Fig. 5b). Taking the increase in the leachable Fe fraction to be about 1.5% (from near 2% to 3.5%), and a SPM content of 50 mg dm^{-3} , we calculate that $13 \mu\text{M}$ Fe had to be removed from the water phase to account for this increase. This amount is a factor of 2 to 3 higher than the decrease in the dissolved Fe concentration ($\sim 5 \mu\text{M}$) observed in the upper estuary. Other processes such as resuspension of Fe-containing bottom sediments might explain the remaining part.

Like Fe, Mn is strongly affected by the redox conditions (Fig. 6). This phenomenon was described extensively by Duinker et al. (1979b, 1982a) and Wol-

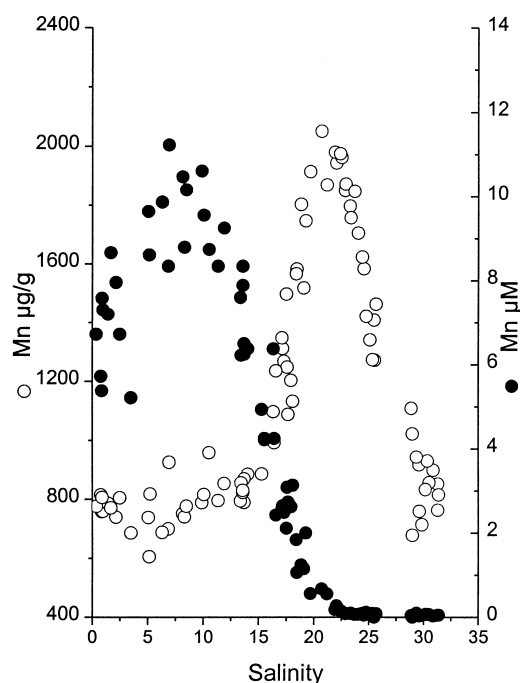


Fig. 6. Dissolved Mn (μM) and particulate Mn ($\mu\text{g/g}$) in relation to salinity.

last et al. (1979), so only a short summary of our results is given here. As soon as the oxygen concentration increases, at salinity 15, Mn is oxidised, removed from the water phase and precipitated as oxyhydroxide coatings on suspended particles. This is indicated by a total particulate Mn increase from $800 \mu\text{g g}^{-1}$ up to $2000 \mu\text{g g}^{-1}$ between $S = 15$ – 20 (Fig. 6).

In contrast to Fe and Mn, Cr behaves more or less conservatively as pointed out by Regnier and Wollast (1993) and Salomons and Eysink (1981). This is confirmed by the data in Fig. 7a, showing that the Cr/Al ratio in the SPM is correlated with mass of SPM. The Cr distribution resembles the mixing profile of fluvial mud (Fig. 7b) supporting its conservative behaviour. This is also reflected in the leachable Cr fraction, which is more or less constant (20–30%) over the entire estuary (Fig. 7b).

The mixing curve of Pb is completely different from those of the other metals. Up to a salinity of 15, total particulate Pb concentrations are more or less constant at 100 to $150 \mu\text{g g}^{-1}$ and then increase to ~ 400 to $600 \mu\text{g g}^{-1}$ at higher salinity with the

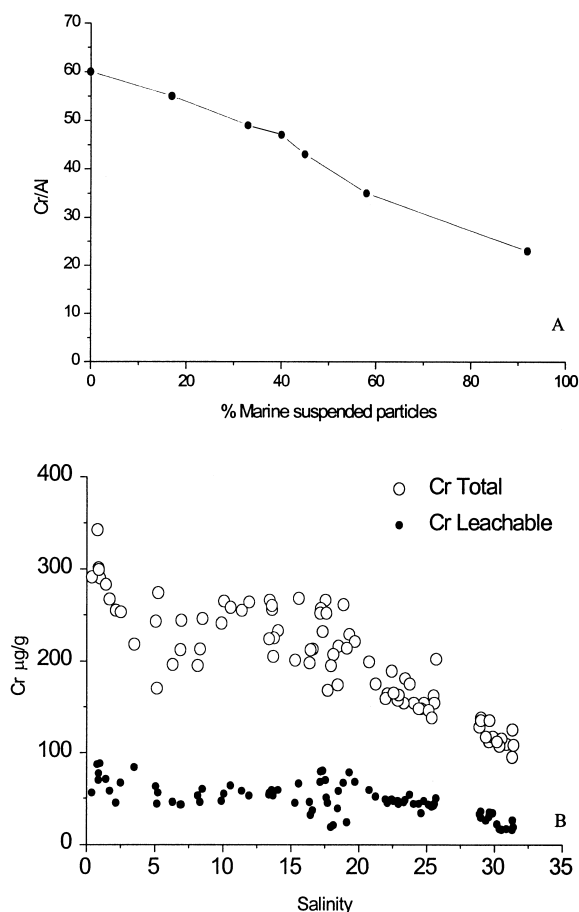


Fig. 7. (A) The Cr/Al ratio in relation to the amount marine suspended particulate matter, and (B) total and leachable fraction of Cr ($\mu\text{g/g}$) in the SPM.

largest fluctuations at $S \sim 30$ (Fig. 8a). This is in contrast to the recent observations of Regnier and Wollast (1993), Baeyens et al. (1998b) and Zwolsman and Van Eck (1999), who reported decreasing Pb concentrations with increasing salinity. However, Wollast (1988) reported Pb concentrations varying from 30 to 150 $\mu\text{g g}^{-1}$ in sediments in the upper estuary with the lowest values in the upper part of the estuary. Taking into account the increase of the Pb/Al ratio at higher salinity (not shown), it is unlikely that small inorganic particles with a high Pb content alone explain our observations. An alternative explanation of the increases in the dissolved

(Fig. 8b) and particulate Pb fractions (Fig. 8a) may be external inputs for which there are three possibilities. (1) Lead-enriched material derived from the tidal flats, (2) an atmospheric source that results in a significant increase in particulate Pb (w/w) at $\text{SPM} = 30 \text{ mg dm}^{-3}$, or (3) local pollution sources. If local inputs were the dominant source then the fact that the higher Pb concentrations in the SPM were not detected 12 and 17 years later by Regnier and Wollast (1993) and Baeyens et al. (1998b) could mean that these inputs are now absent or diminished. We have to keep in mind that during this study all SPM samples were collected by filtration. The more recent SPM samples were obtained by centrifugation, and this difference in sampling techniques could also explain part of the discrepancy in the Pb data. Filtration removes the smallest particles with large surface areas and possibly high Pb and Cu content from the water phase, while this fraction probably escapes the centrifugation, and therefore may not have been detected.

The Cu content in the SPM illustrated in Fig. 8c shows decreasing concentrations in the upper and mid-estuary. Mixing of marine particles with low Cu content with those of fluvial origin is the main factor that controls this distribution pattern. The very constant leachable fraction of 60 to 80% in the major part of the estuary supports this observation. Superimposed on this, particles with a higher Cu content, equal to the Pb observations, are present in the lower estuary. The conservative Cu/Al ratio (not shown) at $S < 20$ indicates physical mixing of particles with different Cu content and implies that geochemical processes are of minor importance (Monteny et al., 1993). The observed concentration range (50–300 $\mu\text{g g}^{-1}$) equals those reported by Monteny et al. (1993), Regnier and Wollast (1993), and Zwolsman and Van Eck (1993). However, none of these authors detected a higher Cu content in the SPM in the lower part of the estuary. In contrast, Duinker and Nolting (1977) observed in 1975 an increase in the SPM-Cu content from 200 to 400 $\mu\text{g g}^{-1}$ in the mid-estuary and a subsequent decrease to 200 $\mu\text{g g}^{-1}$ at $S 25$.

Dissolved Cu concentrations (Fig. 8d) vary significantly in the freshwater and estuarine section without distinct trends. Oxidation of metal sulphides from resuspended sediments in the oxic part of the

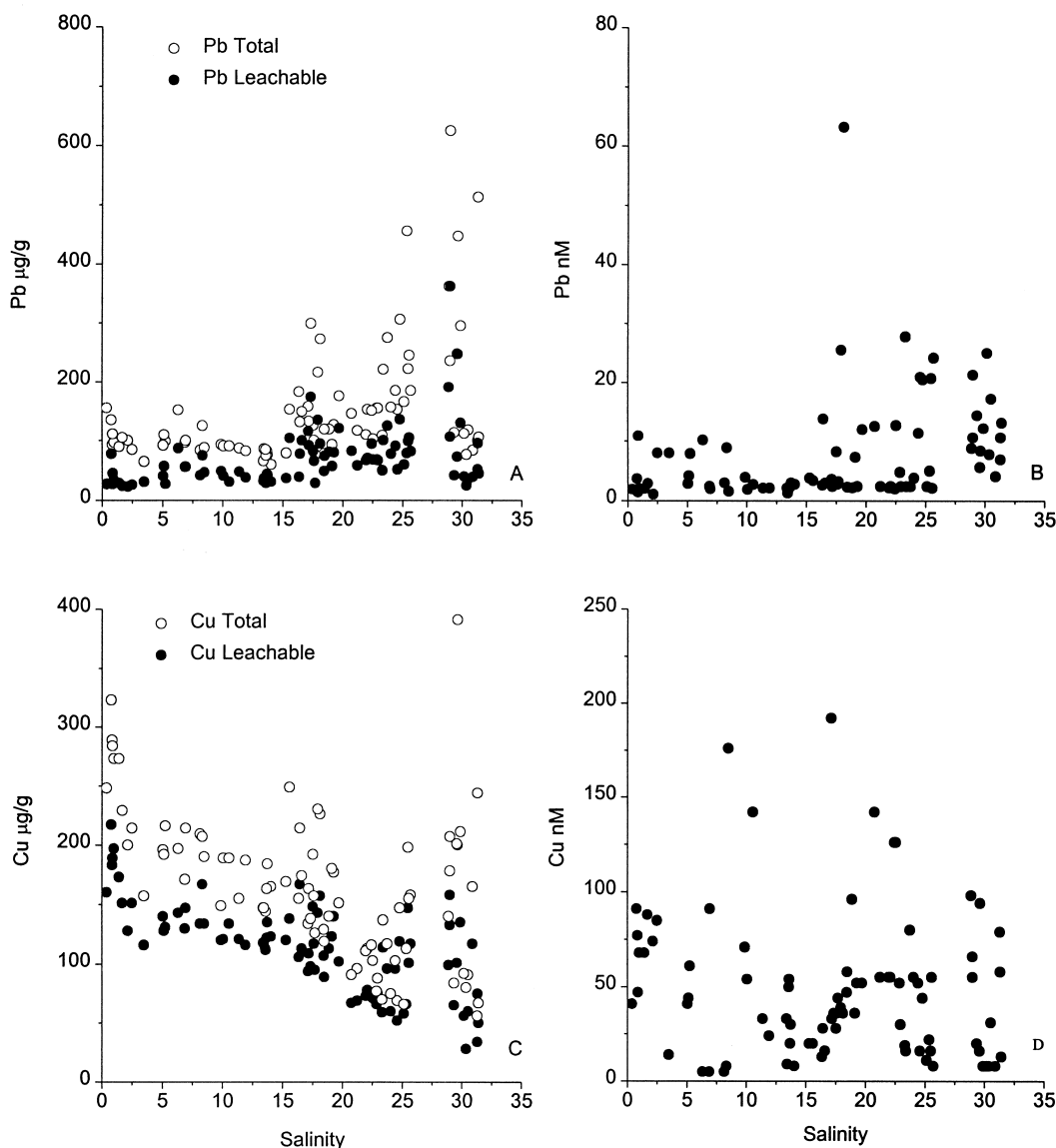


Fig. 8. (A) Total and leachable fraction of Pb in SPM, (B) dissolved concentrations of Pb, (C) total and leachable fraction of Cu in SPM, and (D) dissolved concentrations of Cu as function of salinity. Data from all stations.

Scheldt may contribute to this patchy pattern. Copper concentrations varying from 5 to 82 nM over an annual period at a fixed station near Hansweert (km 60) in 1993 were reported by Gerringa et al. (1996a,b). Higher dissolved Cu concentrations at a salinity of 17 were also reported by Monteny et al. (1993), Zwolsman and Van Eck (1993) and Baeyens et al. (1998b). Duinker and Nolting (1977)

reported dissolved Cu concentrations of 47 nM in the lower part of the estuary in 1975. All these observations indicate that the variation in the dissolved Cu concentrations is large and strongly depends on current velocity and hence tidal phase. Variations in dissolved Cu may be explained by variations in dissolved organic ligand concentrations as shown by Van den Berg et al. (1987) and Gerringa et al. (1998).

3.5. Comparison of 1978 with the present situation

At present the extension of the anoxic part of the river Scheldt is significantly smaller than in 1978 (Fig. 3). In summer, it presently extends to a salinity of ~ 7 and during winter with high river discharges there is no anoxic zone in the upper part of the estuary at all (Zwolsman and Van Eck, 1993; Zwolsman et al., 1997; Baeyens et al., 1998b). This has consequences for the behaviour and distribution of metals, especially for redox controlled metals (Duinker et al., 1982a). The effect of the shift of the anoxic zone to lower salinity is illustrated by the dissolved and particulate Mn distributions. While in 1978 the dissolved and particulate peaks were observed at $S \sim 10$ and $S \sim 22$, respectively (Fig. 6), these maxima have moved to $S < 10$ and $S \sim 15$ at present (Paucot and Wollast, 1997).

Also the dissolved Zn maximum which was observed at $S \sim 18$ during our study in 1978 has shifted to $S < 10$ (Fig. 9a), both in summer and winter (Zwolsman et al., 1997; Baeyens et al., 1998b). Thus, now the mobilisation of Zn occurs in a smaller area than in the past. This may, together with the reduced trace metal loads, explain the lower dissolved Zn concentrations measured by Zwolsman and Van Eck (1993), Zwolsman et al. (1997) and Baeyens et al. (1998b).

For dissolved Cd (Fig. 9b) the shift is more dramatic. In 1978 the dissolved Cd concentration started to increase at salinity > 15 and a clear maximum was observed at $S \sim 20$. At present a broad dissolved Cd plateau at 1 nM is found between salinity 5 and 30 and concentrations are significantly lower (Zwolsman et al., 1997; Baeyens et al., 1998b). Comparing the present situation with the past, we conclude that the area of Zn mobilisation is restricted to lower salinity ranges at present and that Cd mobilisation starts at salinity 5 compared to 15 in 1978, and continues over a longer salinity range. The differences in mobilisation of Zn and Cd may be explained by the slower kinetics for oxidation of Cd sulphides than of Zn sulphides. This different behaviour will be described separately in detail by Gerringa et al. (in prep.), using model calculations from both data sets.

For dissolved Cu we did not find a clear maximum in the estuary, but concentrations were significantly

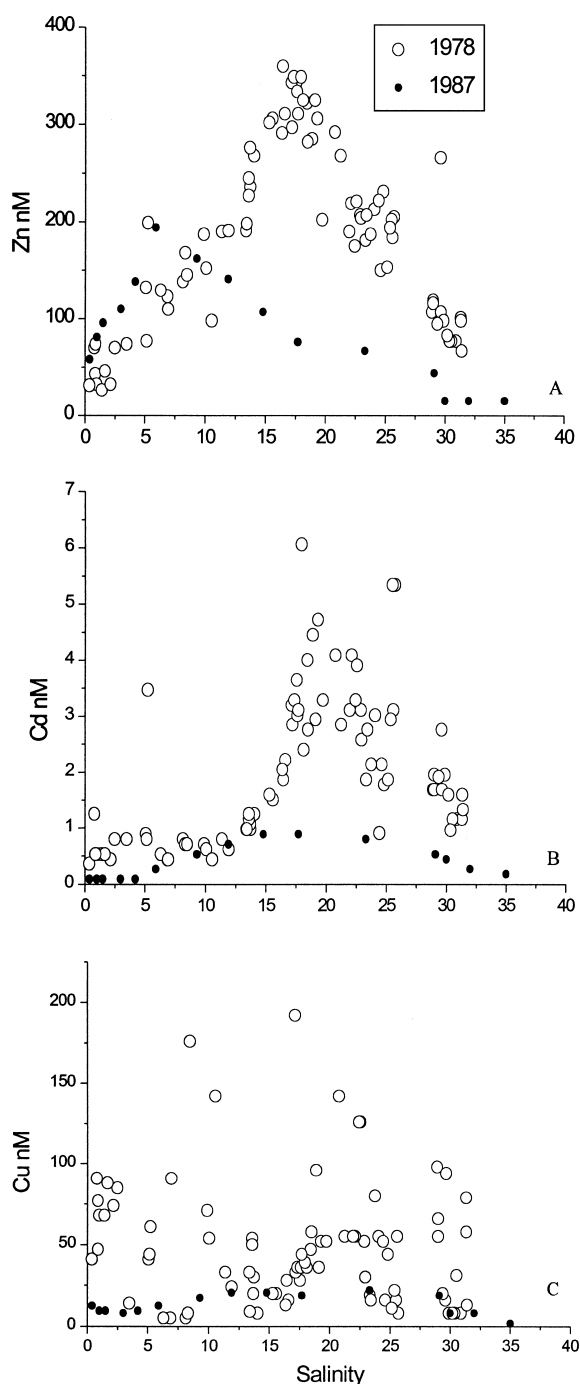


Fig. 9. The maxima and dissolved concentrations of (A) Zn, (B) Cd, and (C) Cu in the Scheldt estuary against salinity in 1978 (this study) and in 1987 (data Zwolsman et al., 1997).

Table 1

Historical overview of trace metal contents of suspended matter in the river Scheldt normalised against Al. Samples collected in the upper estuary

Element/Al $\mu\text{g}/\%$	Ref. 1 1991–93 $n = 8$	Ref. 2 1993 $n = 1$	Ref. 3 1988–89 $n = 3$	Ref. 4 1987 $n = 8$	Ref. 5 1978 $n = 1$	This study 1978 $n = 14$
Cd	2–3	3	2	3	10	9 ± 2
Cu	30–40		35	48	49	53 ± 10
Zn	100–200			233	260	263 ± 45
Pb			35	46	72	23 ± 6
Ni	10–12	10	8	14	24	34 ± 6
Cr	30–40		40	64	70	60 ± 7
Mn	200	200		194		173 ± 13

Ref. 1. Paucot and Wollast, 1997. Ref. 2. Paucot and Wollast, 1996. Ref. 3. Regnier and Wollast, 1993. Ref. 4. Zwolsman and Van Eck, 1993. Ref. 5. Salomons and Eysink, 1981 (Al, 5.56%).

higher in 1978 (average 50 nM) than those reported recently: 10 to 30 nM (Zwolsman and Van Eck, 1993; Zwolsman et al., 1997; Paucot and Wollast, 1997; Baeyens et al., 1998b). In Fig. 9c the results of 1978 and 1987 are compared. The Cu pattern in 1987 follows the observed trend of Cd, mobilisation above salinity 5, but for 1978 no trend was observed.

Few data on dissolved Pb were published for the Scheldt estuary until recently (Baeyens et al. (1998b). The higher concentrations detected in the lower estuary during our study were not observed by the latter authors in 1995. Whether this has something to do with reduced emissions is difficult to prove, but it is clear that the dissolved Pb concentrations were significantly lower (0.5–1.0 nM) during the 1995 surveys than the values reported in the present study. Table 1 gives a historical overview of trace metal concentrations normalised against Al in SPM collected in the upper part of the estuary. It shows that Cu and Mn concentrations remained more or less constant from 1978 to 1993, but that Cd, Cr, and Ni and to a lesser extent Zn concentrations decreased significantly. Although these data are based on different sampling periods, and the fluvial end member value is not constant throughout the year (Zwolsman and Van Eck, 1993), they indicate that the total trace metal load in the river Scheldt diminished significantly in the 1978–1993 period. The recently reported data by Baeyens et al. (1998b) are not included in the table because normalisation against Al was not possible. Comparing their recent 1995 data with those of 1978, we conclude that

especially in the upper estuary the Cu, Cd and Zn concentrations are now significantly lower. In the lower estuary these differences are smaller.

3.6. K_d values

In order to study the particle–water interactions along the estuarine zone, distribution coefficients K_d ($\text{cm}^3 \text{g}^{-1}$): $K_d = P/C$ where P is the particulate concentration ($\mu\text{g g}^{-1}$) and C dissolved concentration (ng cm^{-3}), were calculated for both the leachable (reactive) fractions and total element contents at different salinities (Table 2). These calculations show that K_d s of Cu, Cd, Zn and Pb decrease, and that those of Ni, Fe and Mn increase with salinity, and hence with oxygen concentration and pH (Paucot and Wollast, 1997). K_d values for the exchangeable fraction of Cu, Pb and Ni (Table 2) follow the same trend as the K_d s for total metal contents. Thus, because the non-reactive component is relatively constant throughout the estuary, exchange processes during estuarine mixing are sufficiently reflected in the K_d values obtained for total concentrations. Turner et al. (1992) came to the same conclusions for the river Weser.

In Fig. 10 the K_d values based on total concentrations are presented against salinity. From Table 2 and Fig. 10 it is evident that the distribution between solid and dissolved phase cannot be represented by one single value due to changing redox conditions as was also shown by Paucot and Wollast (1997). The K_d for Fe, for example, increases sharply up to a salinity of 15 and stays constant at higher salin-

Table 2

Trace metal log K_d values in different river systems and the ocean

	Salinity	Cu	Cd	Zn	Pb	Ni	Fe	Mn
<i>Scheldt</i> (This study)								
Total	1.5	4.8	5.8	5.5	5.3	3.9	5.4	3.3
	5	4.8	5.2	5	5.2	3.9	6.1	3.1
	10	4.7	5.5	4.9	5.2	3.9	6.4	3.2
	15	4.5	4.7	4.6	4.8	4.1	6.9	3.6
	20	4.5	4.7	4.6	4.8	4.3	6.9	4.8
	25	4.8–4.9	4.6	4.5	5	4.5	6.9	5.4
	30	4.5	4.4	4.6	4.9	4.9	6.9	5.6
Exchangeable	1.5	4.6		5.4	4.9	3.6	4	3.2
	15	4.4		4.5	4.6	3.7	6.4	3.5
	30	4.3		4.5	4.6	4.6	6.4	5.5
Paucot and Wollast, 1997								
Low	4.7–5.7	5.2–6.3	4.6–5.2		3.5–3.9			
High	4.2–5.6	3.9–5.3	4.3–4.6		3.8–4.2			
Monteny et al., 1993								
	1.5	5.1		4.6				
	15	4.7		4.4				
	30	4.4		4.6				
Valenta et al., 1986								
	15	5	4.5		6.2			
<i>Weser</i> , Turner et al., 1992								
Total	0–30	4.1	4.1	4.8	6.2	4.3	7.4	5.5
Exchangeable	0–30	3.6		4.6	5.8	3.7	6.6	5.5
<i>Humber</i> , Turner et al., 1993								
	1.5		3.5	3.9			3.9	
	30		2.9	4			5	
<i>Rhine</i> , Salomons et al., 1981								
	1.5		3.5	3.3				
	30		2.7	3.5				
<i>North Sea estuaries</i> , Balls, 1989								
		4.0–5.0	3.5–5.0	4.0–5.0	5.0–7.0	4.0–4.5		
<i>Hudson</i> , Li et al., 1984								
	1.5		4.2	4.1				
	30		3.6	3.2				
<i>Oceans (surface water)</i> , Valenta et al., 1986								
		6.1	4.5–4.9		6.3–6.5			
<i>Atlantic Ocean (surface)</i> , Helmers, 1996								
		4.5–5.9	5.1–6.2		4.7–6.4			

ity. The K_d for Mn remains constant to a salinity of 20 and increases more than one order of magnitude at higher salinity. These changes in K_d are caused by the oxidation of dissolved (reduced) Fe

and Mn in the water column and formation of solid (hydroxy)oxides, first the kinetically more rapid Fe, followed by Mn at higher oxygen concentrations in accordance with known redox sequences (Froelich et

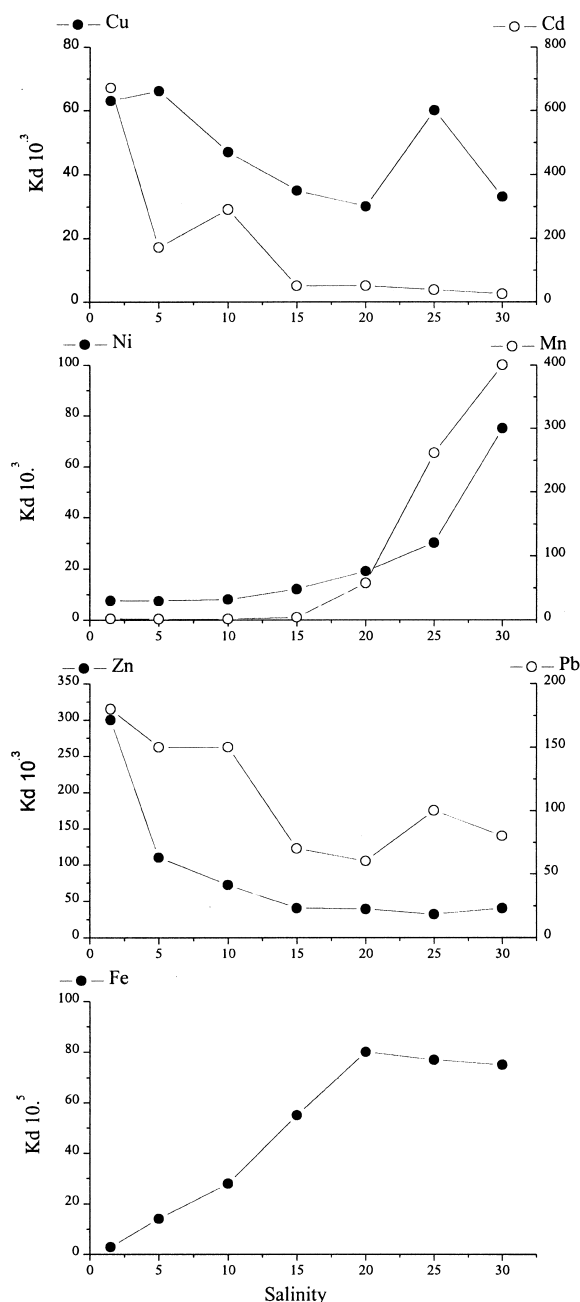


Fig. 10. K_d values of Cu, Cd, Mn, Ni, Zn, Pb and Fe calculated for distinct salinities along the Scheldt estuary.

al., 1979). The K_d values of Zn, Cd, Pb and Cu show more or less the reverse behaviour of Fe; high K_d values in the low salinity range, decreasing between $S = 10$ – 15 due to oxidation of sulphides and mo-

bilisation, and then remaining constant at $S > 15$. The K_d decrease of Cd is orders of magnitude lower in the early stages of mixing. Ni follows the pattern of Mn, oxidation and removal between salinity 15 and 20, although the increase is not so dramatic. These observations confirm the strong correlation between Ni and Mn in the Scheldt estuary described by Zwolsman and Van Eck (1993).

Our mean K_d values are in line with those reported for Cu, Cd, Ni, Mn and Zn by Paucot and Wollast (1996, 1997), for Cu by Valenta et al., (1986) and Monteny et al. (1993), and for Cd by Turner (1996) (Table 2). The K_d values of Paucot and Wollast (1997) with higher values for Cu, Cd, Zn and lower values for Ni at low salinity may be due to the existence of small zones of low oxygen concentrations in the upper estuary to salinity 5–7, compared to $S = 15$ in 1978. However, apart from redox reactions, an important factor determining dissolved Cu is the dissolved ligand concentration (Van den Berg et al., 1987; Gerringa et al., 1996a,b). This is to a lesser extent also true for Zn. Zn shows a contrasting behaviour in different studies: decreasing K_d with increasing salinity (this study), no change with salinity (Monteny et al., 1993), and an increase with salinity in the Weser estuary (Turner et al., 1993). A closer look at the K_d values for Zn in our study shows an almost linear change with salinity in the anoxic zone. Apparently Zn is mobilised/oxidised already at low oxygen concentrations.

Turner et al. (1992) reported the sequence of magnitude for K_d s from the Weser estuary as follows: Fe > Mn, Pb > Zn > Ni > Cd, Cu. This sequence was based on one value over the whole salinity regime, not taking redox affects into account. Only at a salinity of 30 in the Scheldt estuary is the sequence similar to those given by Paucot and Wollast (1997) and to what was found for the Weser by Turner et al. (1992) (Table 3).

Turner et al. (1992) showed that K_d values depended on SPM concentrations in the Weser estuary, with higher values for Cu, Pb, Zn and Ni at low suspended load, whereas in the Scheldt estuary the highest values for Cd, Cu, Pb and Zn were at higher suspended loads. Normally trace metal concentrations in SPM are lower in the high turbidity zone due to mixing of fine fluvial particles with high trace metal content and coarse particles with low trace

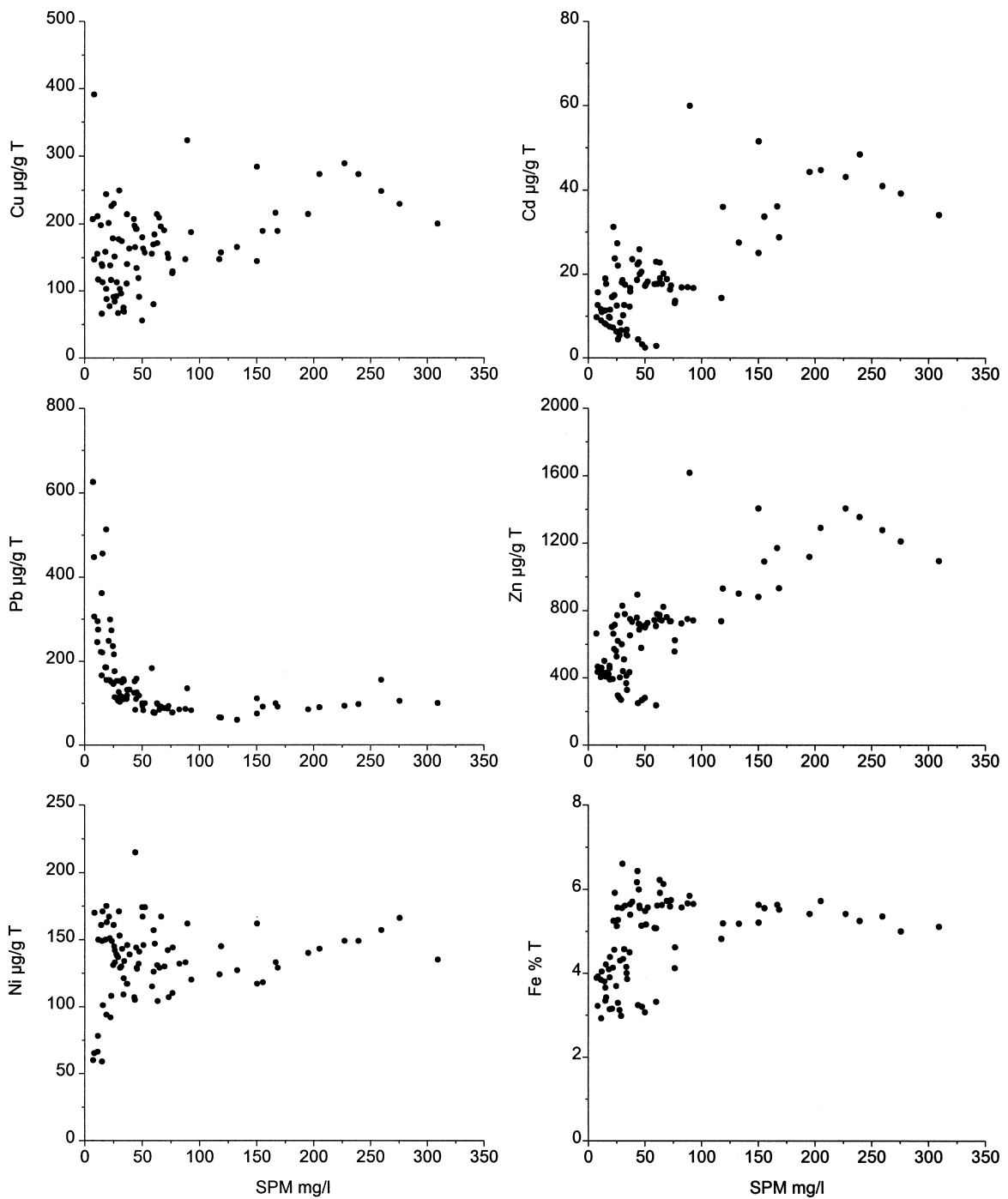


Fig. 11. Total concentrations of particulate Cu, Cd, Pb, Zn, Ni ($\mu\text{g g}^{-1}$) and Fe (%) as function of the amount of suspended matter (mg dm^{-3}).

Table 3

Sequence and magnitude of K_d values as a function of salinity in the river Scheldt

Salinity	K_d			
	10^6	10^5	10^4	10^3
1.5		Fe, Cd, Zn, Pb >	Cu >	Ni, Mn
5	Fe	Cd, Zn >	Pb, Cu >	Ni, Mn
10	Fe >	Cd, Pb >	Zn, Cu >	Ni, Mn
15	Fe >		Cd, Ni, Zn, Cu, Pb >	Mn
20	Fe >		Pb, Mn, Cd, Zn, Cu, Ni	
25	Fe >	Mn, Pb >	Cu, Cd, Zn, Ni	
30	Fe >	Mn >	Pb, Ni, Zn, Cu, Cd	
<i>In the Weser, Turner et al. (1992):</i>				
	Fe >	Mn, Pb >	Zn > Ni > Cd, Cu	

metal contents. This appeared not to be so in the Scheldt estuary in 1978. We believe that the high degree of contamination in the Scheldt in 1978 was responsible for this peculiar situation, as can be evidenced by plotting the trace metal content in the SPM against the concentration of SPM (Fig. 11). These plots show that with increasing concentration of SPM the Cd, Cu and Zn concentrations in the SPM increase as well. Only Pb shows the pattern normally observed in moderately polluted estuaries (Duinker et al., 1982b).

4. Conclusions

High concentrations of Cu, Cd, Zn, Ni and Cr were detected in the SPM in the upper estuarine part of the Scheldt in 1978. Due to the mineralisation of the high organic load in 1978, anoxic conditions extending to salinity 15 were found in the upper part of the estuary. This anoxic zone had a significant impact on the redox chemistry of dissolved and particulate trace metals. At present the heavy metal load in the river Scheldt has decreased considerably, and, as a consequence of the reduced anthropogenic organic load, the anoxic zone has shifted in an upstream direction. This shift affects the dissolved trace metal distributions significantly, and has moved the mid-estuarine maximum, as observed in 1978, to less saline waters. Also, the zone in which mobilisation takes place has become smaller than in 1978 and now extends to salinity 7. There are numerous processes regulating particulate trace metal concentrations, but

the main factor controlling the metal gradient in the SPM is the mixing of fluvial-derived material with less polluted marine material.

Although K_d values can inform us about the re-distribution of metals between the dissolved- and the particulate phase in estuaries, conclusions about mobilisation/removal processes can only be made if more parameters are taken into account and a range of K_d values covering the whole salinity regime determined.

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